MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963
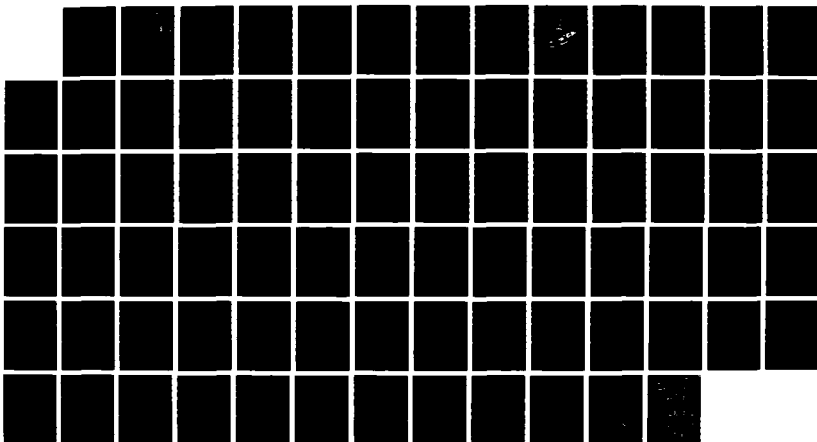
EVALUATION OF THE POTENTIAL HEALTH HAZARDS

ASSOCIATED WITH THE MACHINING OF CARBON FIBER COMPOSITES

by

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A technical report submitted to the faculty of the
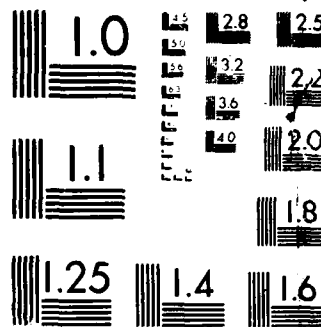University of North Carolina at Chapel Hill in partial
fulfillment of the requirements for the degree of Master of
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ABSTRACT

Industrial hygiene surveys were conducted to assess
personnel exposures to carbon fibers and carbon/epoxy
composite dust during carbon composite airframe sanding
operations. The operation is currently performed every two
to three weeks for eight hours at a time. The nature and
frequency of operation performance is expected to change as
more composite aircraft are put into service. Survey
results showed that actual exposures ranged from 0-<.07
fibers/cc for carbon fibers and 1.25 mg/m^3 to 2.81 mg/m^3 for
total composite dust. Chamber sampling of "worst case"
exposures ranged from 0-.5 fibers/cc for fibers and 31.9
mg/m^3 to 96.62 mg/m^3 for total dust. The health
implications of carbon composite particulate exposure are
not well understood. Good industrial hygiene practices,
however, suggest that exposure levels be kept to a minimum.
Recommendations for reducing personnel exposure have been
made.

To characterize the composite debris, a particle size
distribution and fiber dimension analyses were done.

Additionally, several organizational standards relating
to carbon composite particulates were evaluated. A

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recommendation for reducing the applicable Coast Guard
standards has been made.

Other potential hazards identified were exposure to
solvents during lay-up procedures, and to primer dust during
sanding work. Both require further evaluation to determine
the extent of the exposure.

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ACKNOWLEDGEMENTS

I. INTRODUCTION

Operation

With the discovery of the carcinogenicity of asbestos, public health professionals are beginning to examine the possible toxic effects of other fibrous materials. It was for this reason that supervisory personnel at the U.S. Coast Guard Aircraft Repair and Supply Center in Elizabeth City, North Carolina became concerned with carbon fiber composite machining operations being performed at their facility.

The Coast Guard's HH-65A aircraft is a helicopter that is manufactured in France by Aerospatiale. The Coast Guard currently has 55 of the aircraft in service, with 41 more to be delivered (1). The HH-65A is an exceptional aircraft because it is composed of such a large percentage of composite materials (Figure 1). Approximately 80% of the hull and other components of the HH-65A are composites of various types. About 50% are carbon composites.

The carbon composites in the HH-65A are of high strength and moderate modulus. These mechanical properties are common to aerospace composites. A polyacrylonitrile-based carbon fiber reinforcement and an epoxy resin matrix comprise the composite (1).

Figure 1

Carbon
Glass
Metal-Nomex material
Kevlar
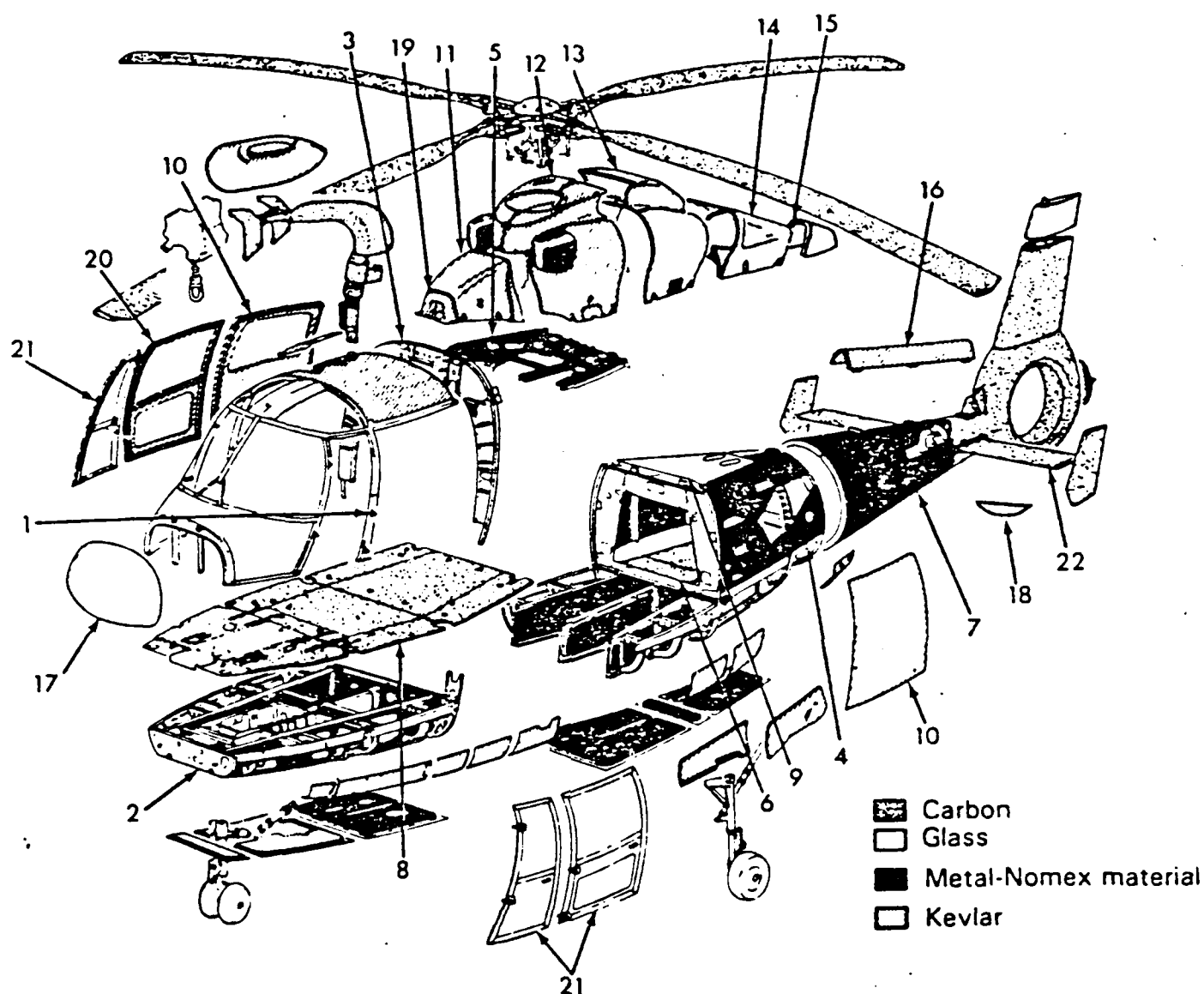
As the composite components require maintenance or repair, they are shuttled through the hull rework section at the Aircraft Repair and Supply Center where they are ground and/or sanded. The machining operation has been done in the past in an open area in a large hangar, but is currently being performed in the fiberglass shop, a 30 ft. by 50 ft. enclosed space. The sanding is done by one or two civilian employees using high-speed pneumatic sanders. The sanding/grinding operation itself either involves the direct gouging of the carbon composite or sanding of carbon composite components lightly coated with a metal-free polymer.

Machining is now performed every two or three weeks for a full 8-hour day by two workers. As the remaining aircraft are delivered and the others begin to age, the frequency of the operation is expected to increase.

Objective

Reports from workers and supervisors indicate that dust levels generated during machining operations are very high (2). · Corrective measures taken to minimize employees' exposure have been unsuccessful. The purpose of this report is to characterize worker exposure to carbon composite debris and recommend controls to limit that exposure. In this regard, the nature of the particles generated during the operation will be analyzed. Further, the Coast Guard standard governing the operation will be evaluated.

Composite Materials

The term composite can mean many things to many people. Generally, a composite is a material made up of more than one component. More specifically, to a materials engineer a composite is a material in which some type of reinforcement is embedded in some type of matrix. Synergy is also a key quality of a composite material. The composite is expected to have mechanical properties which are superior to those of its individual components (3).

The manufacture and use of composite materials by man is not a recent development. The ancient Egyptians and Chinese embedded straw in bricks to improve their structure. Reinforced concrete has been a standard material in the construction industry for decades (4). The modern era of composite materials began in the 1950's spurred by the need for new structured materials that were strong, tough and lightweight. Conventional engineering materials, metals and alloys, are strong but not light. Certain covalent materials are strong but not tough, and most plastics are light but lack strength and toughness. The early development of composites of carbon and glass fibers produced structural materials that were strong, stiff, low-density and resistant to failure at high temperatures. Since that time, the varieties and uses of composites have grown sharply (4).

Many types of composites now exist and many more are being developed with increasingly complex structures and

capabilities. This is due to the multitude of materials that components- matrices, reinforcements, and additives- are made of, and the differing processes used to fabricate these materials into parts (4). The physical characteristics of a composite are determined by the characteristics exhibited by its component parts (5). Fibers employed in composites include carbon, glass, boron and ceramics. Matrices may be metal, ceramic, organic polymers, or bulk carbon. Hundreds of different materials may be used as additive fillers in composites. The more commonly used fillers are talc, calcium carbonate, kaolin, wood, flour and mica. While fillers are generally used to reduce costs they can also add many useful properties to the composite such is compression strength, dimensional stability, and thermal and electrical qualities (3).

The evolution of composites has spawned a group of composites known as advanced composites. Generally speaking, these are composites whose outstanding strength-to-weight properties make it possible to do things that otherwise could not be done.

The aircraft/aerospace/military market is the fastest growing market for advanced composites, increasing its use by 12% in 1986 (6). These related industries have many reasons for their utilization of composites. The high specific stiffness of carbon fiber reinforced plastic composites makes them well-suited for maintaining shapes in wing spoilers and rudders. When high strength is integrated

into the composite, the material is useful for aircraft
wings, tail parts, and helicopter rotor blades (7). The
National Aeronautics and Space Administration (NASA) has
experimented heavily with the use of composites in aerospace
structures and has determined that the next generation of
aerospace systems, through the use of carbon composites,
will provide benefits in the form of reduced weight, size,
cost and improved performance (8). It should be noted that
the purchase price of composites exceeds their monolithic
counterparts. Advanced composite systems now in use cost
about $30 to $60 per pound, and experimental composites cost
$100 to $200 per pound. It is through reduced fuel
consumption, maintenance, and part replacement that
composites reduce cost in aerospace applications.

Carbon Fibers

The fiber component in the composite used in the
airframe of the HH-65A is the carbon fiber Torayaca T-300
made by Toraya of Japan. The Torayaca T-300 is a
polyacrylonitrile precursor fiber, and has a diameter of 7
microns. The fiber has high strength and moderate modulus
(1,9).

Carbon fibers are by far the most widely used
reinforcement currently being used in advanced resin matrix
composites because of their unique mechanical properties.
Carbon fibers are strong, stiff, and most importantly,
lightweight. The high strength of the fiber can be

attributed to the anisotropic nature of the graphite crystal. In turn, the strength of the graphite crystal is based on the strength of the carbon-carbon covalent bonds in the crystal. Carbon is also lightweight, among the least dense of the elements, and abundant in nature, and hence potentially inexpensive (10).

Another reason for the trend towards carbon fiber use are the environmental health concerns associated with asbestos. Because of its superior inherent mechanical properties, asbestos was chosen over carbon fiber for many specific applications. The documentation of cases of serious chronic diseases such as pulmonary fibrosis, mesothelioma, cancer of the bronchus, and other tumors, however, has initiated a search for safer substitutes (11). Many organizations, including the Coast Guard have begun programs to completely eliminate asbestos and asbestos-containing materials from their inventory (12).

The current technology for producing carbon fibers is based on the thermal decomposition of organic precursors. Materials as diverse as rayon, polyacrylonitrile (PAN), pitch, polyesters, polyamides, and various resins have all been considered as precursors in carbon fiber production. Through extensive research, rayon, PAN, and pitch have been determined to offer the greatest potential.

Investigations into the use of organics as a precursor for carbon fiber began as early as 1880 when Thomas Edison pyrolized regenerated cellulose fibers in producing carbon

filaments for his incandescent lamp. The processing of carbon fibers in filaments developed until about 1909 when flexible tungsten filaments became available. Tungsten soon became preferable to carbon and the use of carbon filaments fell significantly (13).

A renewed interest in fibrous carbon came about as a result of the emergence of the aerospace program in the United States. Super refractory reinforcing agents to be used in ablative composites for rockets were produced by Salter and Abbott who converted natural cellulose and rayon into carbon fiber. These fibers were produced by heating the precursors at temperatures of $1000^{\circ}C$ in inert atmospheres.

A considerable amount of work was done in developing fibrous carbon between 1959 and 1964. Refinements in production procedures made carbon fibers less expensive and mechanically stronger, but its overall mechanical properties were still inferior to those of other natural and synthetic fibrous reinforcement materials, such as asbestos and fiberglass. Then in 1965, Tang and Bacon discovered that the key to strong carbon fibers was the orientation of graphite crystals relative to the fiber axis. Through infrared x-ray and transmisson electron microscopy techniques, it was shown that by stretching the precursor at high temperatures $(2500^{\circ}C)$, plastic deformation occurs which gives the preferred orientation. The resultant fiber was

found to possess mechanical characteristics superior to those of asbestos and fiberglass for many applications (9).

Carbon Fiber Precursors

As stated above, the preferred method for producing carbon fibers is by pyrolizing organic precursor fibers. This technique has several advantages over other graphite-filament formation processes. The pyrolysis of organic precursors is practical because large quantities of fibers with desirable qualities can be manufactured with reproducible results. The pyrolysis method is also much less expensive than the other processes. Additionally, long, thin-diameter flexible carbon fibers, essential for the production of carbon composites are easily obtainable through pyrolysis (10).

The conversion of polyacrylonitrile to carbon fibers consists of four steps:

1. spinning the PAN precursor
2. stretching the PAN precursor
3. stabilization
4. carbonization

PAN fibers undergo a wet spinning process where the fiber and copolymers and a solvent are spun into a coagulating bath. The fibers are then washed and dried. The molecular structure of the finished carbon fiber is

heavily influenced by variables of the wet spinning process. When observed under an electron microscope, PAN molecules are seen to be grouped together to form fibrils. The conformation of fibrils is that of an irregular helix. It is the fibriller network that gives the carbon fiber its three-dimensionality. Following the wet spinning process, fibers will normally have a round cross-section.

After they have been spun, fibers are stretched. Through stretching, fibrils achieve their preferred orientation. That is, parallel to the fiber axis (Figure 2).

The purpose of the stabilization step in the production of carbon fibers from PAN is to maintain the preferred orientation of the fibrils by preventing the molecules from relaxing after they have been stretched. Stabilization is achieved by cyclization, or the formation of a ladder polymer consisting of strong carbon-carbon bonds. The ladder gives the fiber its stiffness.

Carbonization is the process by which PAN fibers are pyrolyzed until they are transferred into carbon fibers. It is at this stage that the fiber acquires most of its desirable mechanical properties. During carbonization, fibers and slowly heat treated in an inert atmosphere at temperatures of $1000^{\circ}C$-$1500^{\circ}C$. Within this temperature range most noncarbon constituents are removed from the fiber and approximately 50-60% of the original fiber weight is lost. Products driven off during carbonization include
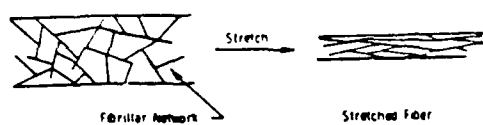
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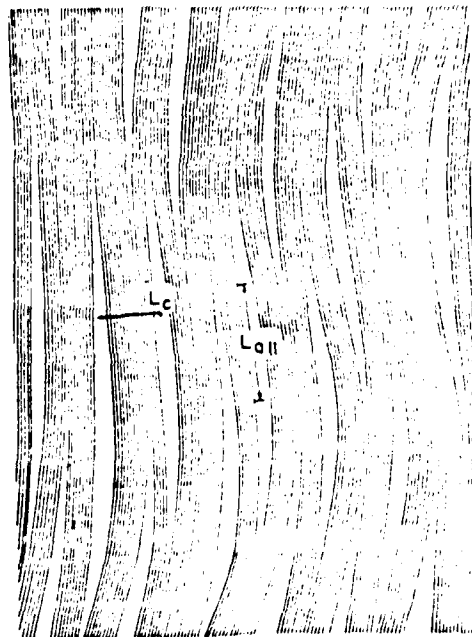
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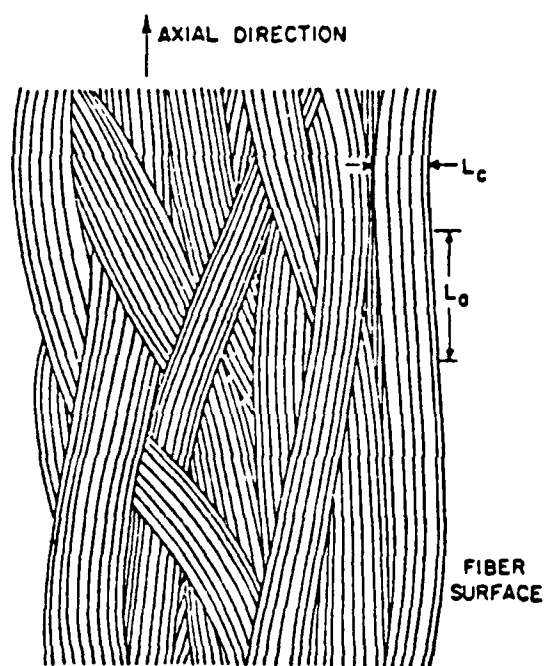
Figure 4

methane, hydrogen cyanide, water, carbon monoxide, carbon dioxide, ammonia and other hydrocarbons. Polynuclear aromatic hydrocarbons are not completely removed during carbonization and therefore remain in the fibers.

At this point it should be noted that a distinction is made between carbon and graphite fibers. The distinction is a minor one, related to the temperature at which the fiber precursor is heat-treated. Carbon fibers generally refer to fibers that are processed at temperatures lower than $1700^{\circ}C$. Graphite fibers undergo a fifth step in the fiber conversion process, graphitization, where the precursor is subjected to temperatures in excess of $1800^{\circ}C$. Graphitization improves the crystallite structure of the fiber and also gives a greater degree of preferred orientation of the graphite-like crystallites within each fiber. This results in mechanical properties which differ slightly from those of carbon fibers. Additionally, due to higher heat-treatment temperatures, 99% of the composition of graphite fibers is carbon, while the carbon content of carbon fibers is 80-95% (10,14).

Structure of PAN Fibers

The basis for the high strength and modulus of carbon fiber is in the anisotropies found within the graphite crystals formed from carbonization. The layer planes of the crystals must also be aligned parallel with the fiber axis. These layer planes are formed from dehydrogenation and

denitrogenation processes which take place during heat
treatment. The removal of hydrogen and nitrogen from the
precursor results in the bonding of adjacent cyclicized PAN
molecules. Extensive bonding results in laterally expanding
sheets which form long ribbons of graphite generally
oriented in the direction of the fiber axis. Several
ribbons combine to form a microfibril. Fourdeux has
postulated that some ribbons run through two or more
microfibrils tying them together (15) (Figure 3). These
microfibrils are, in turn, intertwined in a basketweave
structure to form the carbon fibers (16) (Figure 4).

Epoxy Resins

The matrix material of the carbon composite in the
airframe of the HH-65A is an epoxy resin. Generally, the
term epoxy is applied to compounds containing one or more
oxirane rings. The oxirane ring is a cyclic ether group
which consists of an oxygen atom bonded to two adjacent
carbon atoms. The resultant structure ($C \overset{O}{\diagup\diagdown} C$) is a highly
strained, therefore very reactive functional group. Epoxy
resin compounds contain two or more oxirane rings per
molecule. Epoxy resins are reacted with curing agents
(normally amines) to solidify the epoxy and convert it to a
thermoset plastic (17).

There are several types of epoxy resins. The type used
in the HH-65A is glycidyl epoxy resin derived from

epichlorhydrin and bisphenol A or diglycidyl ether of
bisphenol A (DGBA). DGBA compounds are synthesized in
varying molecular weights. The lower molecular weight
resins are liquids and the higher molecular weight resins
are solids. Epoxy resins used in composites are frequently
mixtures of medium and high molecular weight oligomers of
DGBA (18).

Epoxy resins of higher molecular weight are synthesized
by reducing the epichlorhydrin:bisphenol A ratio. In the
reaction, the initial epoxy groups in the epichlorhydrin and
some of the groups formed by dehydrohalogenation are
consumed (18).

Although more expensive, composite materials with epoxy
resins have many qualities that make them attractive to the
aerospace industry. The shrinkage of epoxy is less than 2%
and no water or other by-product is generated during curing.
Therefore, there is little chance that the epoxy matrix will
separate from the fiber reinforcement and cause the
composite to crack or delaminate. Epoxy-resin composites
also weigh less, are more flexible than other matrix
materials, and have a relatively high tensile strength. The
most desirable quality of epoxy resin as a matrix material,
though, is that they can be tailored to a wide variety of
applications through variations in their chemistry (4).

II. HEALTH AND SAFETY HAZARDS

Carbon Fibers

Carbon fibers are considered biologically inert, as
evidenced by their introduction into the human body as
surgical implants. It is not the chemistry of carbon fibers
that make them potentially toxic to the human body, however,
but its physical nature.

Carbon Fibers-Inhalation

The primary health concern associated with carbon
composite materials is the release of carbon fibers as a
result of grinding, sanding, and cutting. A fiber here is
defined as a particulate with an aspect ratio (length:width)
of at least 3:1. Of the three routes of exposure,
inhalation is the most significant. Most investigators
agree that fibers with a diameter of approximately 3.5
microns or less are potentially the most harmful in that
they are most efficiently deposited in the alveolar region
of the lung, and they exhibit the greatest degree of
biological activity [19]. Stanton has shown that fibers in
excess of 8 microns long with diameters less than 1.5
microns have the greatest biological activity [20]. Most
others agree. This information is the basis of the "long,
thin" hypothesis for the pathogenesis of malignant fibrous

neoplasms. This is where the agreement ends, however. The toxicology of carbon fibers in the human body remains uncertain.

Much research has been done that indicates that carbon fibers pose no significant health risk. In a 1980 NIOSH report, Zumwalde and Harmison cited two animal studies. In experiments done by Holt and Horne, guinea pigs were exposed to high airborne concentrations of respirable carbon fibers fed into a hammer mill apparatus. Examination of the lung tissue found that few particles had reached the lung. No pathological effects on the lung were observed. In a mouse/rat study, one fibro-sarcoma was found. The majority of fibers in both studies had diameters greater than 3.5 microns (21). Zumwalde and Harmison concluded that fibers with diameters greater than 3.5 microns have little effect in producing diseases (22).

In a report for EPA, Wagman et al. studied dusts and residues from the machining of carbon composites. Wagman's group observed that the machining of carbon composites could longitudinally cleave individual carbon fibers thereby reducing fiber diameters below 3.5 microns (23). This may be born out in an analysis of the chemistry of carbon fibers as compared with that of fibrous glass. Glass fibers have amorphous structures and are composed of silicon dioxide. Silica acts as a network former, and is interspersed throughout the fiber. When stressed, as in machining, a glass fiber will fracture transversally because of its lack

of regularity. Carbon fibers, by contrast, are composed of crystallites within a regular network. Under stress, a carbon fiber would seemingly cleave longitudinally along the plane of the weaker ionic bond, not traversely across stronger carbon-carbon bonds (Figure 5) (25). In spite of their finding, Wagman and his colleagues concluded that adverse health effects posed by carbon fibers would likely be limited to skin, eye, and upper respiratory tract irritation (23).

The General Dynamics Corporation sampled airborne particulates around cutting and grinding operations on a carbon composite wing panel. Analysis of the sampled material indicated that less than 8% of the particulate were fibrous, and that less than 20% of the fibers were reduced in diameter. As a result, General Dynamics considers carbon composite particulates merely an innocuous dust hazard (25).

In their Material Safety Data Sheet, Union Carbide, a producer of carbon fibers, warns that temporary eye or skin irritation may occur. Their experiments of chronic, recurrent applications of carbon fiber fragments suspended in benzene to the skin of mice produced weak tumorigenic response (26).

There is also a large body of evidence that suggests that carbon fibers are harmful.

Leineweber puts forth three important determinants for biological activity, and therefore disease causing potential, for fibers:

Transversal   Longitudinal

Fiber Cleaving
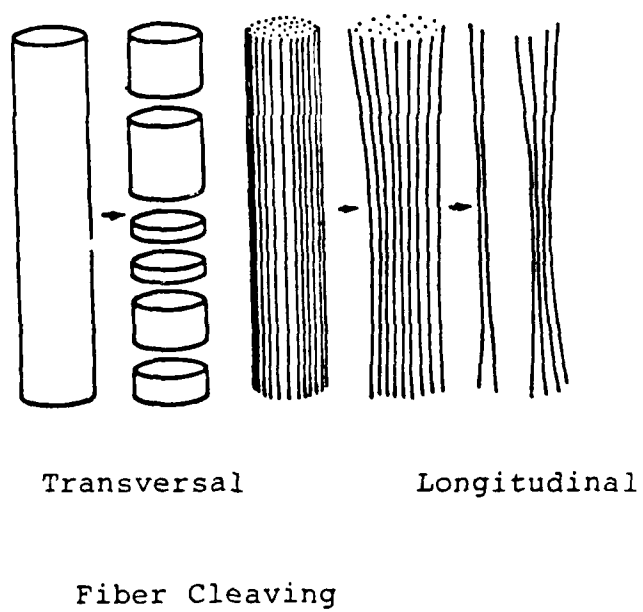
Figure 5

1. dimension of fibers (length and diameter)

2. dose (concentration x duration)

3. durability of the fibers in the biological system

(27)

A model for deposition of fibers in the human respiratory system was developed by Harris and Fraser (28). The model identifies the mechanism of direct interception as being of marked importance in determining the location of fibrous deposition. Direct interception is a mechanism by which a fiber in the respiratory system touches a surface even though a point represented by its center of gravity would pass without touching (29). In the model, direct interception is largely responsible for results that show that as fiber length increases, deposition in the upper respiratory tract increases. The longer the fiber, the greater chance of interception in the nose, and the smaller number of fibers being deposited in the pulmonary region, where they could potentially do the most harm. It is significant to note, however, that although the model shows only 1% of 200 micron fibers reaching pulmonary spaces, this number could be substantial if the dose is high (28). Harris and Fraser's model and prediction for long, thin fiber is confirmed in work by Vorwald who has observed fibers 200 microns in length or greater in the pulmonary region (30).

If a sufficient number of fibers reach the pulmonary region and their dimensions satisfy the "long, thin"

hypothesis, they must remain in contact with pulmonary tissue for a considerable period of time in order to cause disease (27). Several reports indicate that long fibers remain in the lung for longer periods than do short fibers (31). In a study done by Bernstein, Drew and Kuschner, rats were exposed to glass fibers of well-defined sizes by intratracheal injection and inhalation. The short fibers (5 microns) were sucessfully phagocytized by alveolar macrophages and cleared while the longer fibers (60 microns) were not (32). Wright and Kuschner performed a similar test with intratracheal injection of guinea pigs, with the results clearly supporting the "long, thin" hypothesis (33).

Morgan et al. exposed rats by inhalation to radioactive asbestos fibers. The rats were then killed and the lungs measured for fiber length distribution. Fibers under 5 microns in length were rarely found while fibers between 60-100 microns were abundant, again suggesting that short fibers are more readily cleared (31).

Carbon Fibers - Dermal

Carbon fibers may come into contact with the skin as a result of direct contact with the composite, skin contact with a carbon fiber contaminated surface, or by deposition of airborne fibers. Although some areas of the skin may be more sensitive to carbon fibers than others, regional deposition on the skin is not as important as it is in the respiratory system.

Skin irritation has been observed among workers in carbon fiber manufacturing and processing plants. A study at such a Russian facility indicated that 24% of the workers had occupational dermatitis characterized by inflammatory eruptions of the skin (34). The pattern of dermatitis that has been observed in carbon fibers is similar to that which occurs in fiberglass workers. It most often occurs in new employees and in most cases is only temporary. Unlike most dermatitis, the skin seems to become desensitized after continued exposure. After a prolonged absence from exposure, however, renewed exposure could again result in irritation (35).

Additionally, a potential hazard exists where fiber breakage in the handling of the composite has occurred. Splinters from fiber breakage can penetrate a worker's skin and become embedded below the surface. Unlike wood splinters, carbon fiber splinters are brittle and easily break into smaller pieces when attempting to remove them with tweezers. Generally, carbon fiber splinters must be cut out (36).

Epoxy Resin (Diglycidyl Ether of Bisphenol A)

Since matrices of carbon composite materials are engineered for desired mechanical properties to satisfy their intended use, it would not be far from the truth to say that no two epoxy resins, and even no two diglycidyl ether of bisphenol A (DGBA), are exactly alike. Because of

this, completely accurate toxicological data on the epoxy resin in the HH-65A are incomplete. Therefore it is necessary to assess the potential health hazard of epoxy resins based on their physical, chemical and toxicological characteristics (37).

Epoxy Resin (DGBA) - Inhalation

All forms of epoxy resins have a low potential for toxicity for all routes of exposure. The toxicity decreases as the molecular weight of the compound increases. Since it is of moderate molecular weight, the DGBA compound in use on the HH-65A therefore is of very low toxicity. Because of its low volatility, few studies have been done on inhalation hazards associated with DGBA. Work which has been documented indicates that no adverse health effects would result from any route of administration. Some epoxy particles may become lodged in the upper respiratory tract where they would be removed by the mucociliary escalator and swallowed. Animal studies have shown DGBA by oral administration is only slightly toxic acutely while sub-acute studies with rats showed reduced body weight and decreased food consumption but no gross or histopathological lesions. Chronic toxicology and carcinogenicity tests for ingestion of DGBAs have largely been negative (18). Oral administration of cured and uncured, solid and liquid epoxy resins in concentrations up to 10% of the diet induced no tumors in rats (38). Chronic studies in epoxy resins could produce few adverse systematic effects (18).

Epoxy Resin (DGBA) - Dermal

Skin contact with DGBAs represent the greatest potential problem. The fact that epoxy resins can cause dermatitis and possibly skin sensitization upon prolonged exposure is well documented. In a study by Hine, a single application of epoxy resins on rabbit skin was non-irritating. When the same resin was applied for two hours per day for 20 days, the rabbit's skin experienced moderate irritation. Prolonged and repeated skin contact, 4 hours per day for 20 days, caused severe irritation (38). Hine has also reported that liquid epoxy resins are capable of inducing skin sensitization in guinea pigs. Additionally, several reports of skin irritation and sensitization in man have been published (38).

The typical lesion is that associated with contact dermatitis. Early manifestations of epoxy resin dermatitis are redness and edema with weeping followed by crusting and scaling. After initial contact, the lesions reduce in size to the area of original point of contact. This lesion persists for 2-10 days and is followed by a rash and scaling (39).

Sensitization may develop after initial contact. Sensitization is characterized by an eczema accompanied by considerable itchiness, usually extending beyond the original point of contact (18).

Following an investigation by Europea factories, Grandjean reported that 43% of all workers handling epoxy

resins had dermatitis, 22% of those classified as severe cases (39).

A by-product of epoxy resin related operations is the irritation and sensitization of skin by solvents used to remove sticky epoxy resins from the skin. Although the practice is not recommended, resins and resin dusts are often difficult to remove, and solvents are used. In addition to creating their own dermal irritation hazard, solvents also may facilitate the penetration of epoxy resin through the skin (18).

Most studies of the carcinogenicity of epoxy resins applied dermally conclude that they are not carcinogenic (40). Results to the contrary are believed to have come from experiments that used epoxy resins which were not carefully analyzed and may have certain impurities. It is orly recently that the effects of impurities in epoxy resins (e.g. epichlorhydrin, butylglycidyl ether, phenyl glycidyl ether) have been documented and steps have been taken to ensure the purity of commercial epoxy resins (18).

The potential for eye irritation is also a concern with DGBAs. Resins of high molecular weight can cause moderate eye irritation. The epoxy resin dust particles generated by the machining of carbon composite can cause mechanical damage to the eye and surrounding tissue (18).

The amine curing agents used with epoxy resins have associated hazards of their own. Curing agents and hardeners are usually more physiologically active than the

resins. They are also more volatile, and skin and eye irritations may occur (18). Since they are in the solid state and used in such small amounts, however, curing agents are not considered a significant hazard during machining operations.

Carbon Dust - Inhalation

Carbon dust should not present a health hazard to exposed workers. As has been stated, elemental carbon is biologically inert. It is the dimensional characteristic, the 3:1 length to width ratio, that makes a carbon fiber potentially harmful. A carbon dust particle generated as a result of sanding, grinding, or cutting does not meet the criteria of a fiber.

From various models of the deposition of spheres in the lung, we know that particles, depending on their size and density, will be deposited in various locations (41). The respiratory system removes these particles through several mechanisms. Nose blowing, coughing, sneezing, and swallowing assist in the removal of particles from the upper airways. The walls of the nasal and tracheobronchial region are coated with mucous. Additionally, the tracheobronchial walls have cilia that transport mucous and the particles they have entrapped to the top of the trachea where they are swallowed (42). There is evidence that the deposition of carbon dust in the respiratory system actually increases the rate of mucociliary transport (43).

Dust in the pulmonary region is cleared via a slightly different mechanism. The mucociliary system is not found in alveolar spaces. Instead, large white blood cells called macrophages phagocytose foreign matter (44). Phagocytosis is more efficient for spheres than for fibrous particles (21).

Fire Hazard

Carbon composites pose a fire hazard in that a carbon composite fire is not easily quenched. Following successful attempts to douse a composite fire with water, carbon dioxide and other fire retardant chemicals, interior combustion temperatures were found to be over $480^\circ C$. Thus, though a fire might appear to be quenched, the interior heat content is sufficient to initiate burning and reflash the fire (36).

Electrical Hazard

Although not a health problem, a significant problem caused by airborne carbon fibers is damage to unprotected electrical equipment. High electrical conductivity of the carbon fibers is the prime factor for the electrical hazard. Small fiber diameter, short length and low density also contribute to the hazard.

Carbon fibers that settle across electrical contacts or circuits can cause resistive loading, shorts, or electrical arcing. Resistive loading is normally associated with low

voltages and can lead to equipment malfunctions. Carbon fibers across contacts can carry high currents at low voltages and cause shorts. The fibers will quickly burn out in the manner of a fuse, but even a momentary short can blow fuses in the equipment or stress the equipment so that it no longer performs within specificat'ons. Single fibers can also initiate arcing between contacts. Once the arc is initiated, it often leads to extensive destruction of the equipment through fire (8).

Electrical hazards can be minimized through the use of ventilation and other controls to be discussed later.

III. STANDARDS

The environmental standards with which this composite
machining operation must comply are those set by the U.S.
Coast Guard. The Coast Guard has adopted the Threshold
Limit Values (TLV) for chemical substances in the work
environment as set by the American Conference of
Governmental Industrial Hygienists (ACGIH) (45). TLVs
represent airborne concentrations of agents to which all
workers may be exposed day after day without suffering
adverse health effects as a result of that exposure. The
ACGIH bases their standards on information available from
industrial experience, experimental human and animal
studies, or a combination of the three (46).

The ACGIH currently has no standard for carbon or
graphite fibers. They do, however, list synthetic graphite
among the nuisance particulates. Nuisance dusts are so-
called because they do not produce significant organic
disease or toxic effects at reasonable levels of exposure,
but excessive concentrations in the work area may
significantly reduce visibility, leave dust deposits in
eyes, ears, and nasal passages, or cause injury to the skin
or mucous membrane through chemical or mechanical action.
The TLV time-weighted average for synthetic graphite is 10

mg/m^3 of total dust, or 30 million particles per cubic foot $(mppcf)^1$ or 5 mg/m^3 of respirable dust. The time weighted average refers to an average concentration for a routine 8-hour workday and 40-hour workweek (46).

The Occupational Safety and Health Administration (OSHA), the governmental agency charged with improving safety and health in general industry, has also established workplace standards.

Like the ACGIH, OSHA has no standards that specifically apply to carbon fibers or dust. The applicable standard that OSHA has promulgated is for inert or nuisance dust, a subcategory of mineral dusts. The standard for nuisance dust is 15 mg/m^3 or 50 mppcf of total dust, and 5 mg/m^3 or 15 mppcf of respirable dust. These values represent 8-hour time-weighted averages (47).

On the basis of their independent research which indicated that carbon fibers pose no chronic hazard, but only an eye and skin irritation hazard, Union Carbide has established a permissible exposure limit of 5 fibers/cubic centimeter for use in their production facilities (26).

In developing standards for their personnel, the U.S. Air Force consults several sources including ACGIH, NIOSH and various toxicology publications. The current standard that deals with operations involving the machining of carbon composites is a gravimetric one. The Air Force treats

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1 Based on impinger samples by light held techniques.

carbon composite particulates as a nuisance dust and has assigned it a TLV of 10 mg/m^3. The gravimetric sample includes respirable fibers, non-respirable fibers and respirable and non-respirable dust (48).

Among organizations contacted, the U.S. Navy has established the most stringent limits on workplace exposure during carbon composite machining operations. Based on a review of available data, the Navy has determined that personal exposures to carbon fibers should not exceed an 8-hour time-weighted average of 3 fibers per cubic centimeter of air, and that total dust, including respirable and non-respirable fibers and carbon composite dusts, should not exceed 3.5 milligrams per cubic meter, also an 8-hour time-weighted average. Further, the Navy recommends a Short Term Exposure Limit of 7 mg/m^3 of air for total dust, and recommends that fiber concentrations never exceed 7 fibers/cc (49). A Short Term Exposure Limit (STEL) is a 15-minute time-weighted average which should not be exceeded at any time during the workday even while maintaining the 8-hour time-weighted average. Additionally, concentrations at the STEL should not be repeated more than four times a day, and there should be 60 minute intervals between exposures at the STEL (46).

The adopted carbon fiber standard is based on an analogy to fibrous glass. The National Institute for Occupational Safety and Health (NIOSH) has recommended a standard for fiberglass of 3 fibers/cc as a time-weighted average for up

to a 10-hour work shift in a 40-hour workweek. The glass fibers should have a diameter equal to or less than 3.5 microns and a length equal to or greater than 10 microns (50).

Although the chemistry of carbon and glass fibers differ, the physical value of the particles are similar. It has been shown that a fiber's physical properties, not its chemistry, are critical in assessing its potential health effects. Therefore, if we can accept the fact that carbon fibers cleave longitudinally as reported by Wagman et al., then the analogy between carbon and glass fibers can be made.

As could be expected, the major hazards reported for fiberglass exposure are dermal, eye and upper respiratory irritation. Occasional cases of bronchitis, pharyngitis, and asthma were reported, along with isolated reports of pneumonia and fibrosis (50).

The Navy's adopted total dust standard is based on an analogy to carbon black. NIOSH has recommended that the carbon black standard be set at 3.5 mg/m^3 (51). Carbon fiber dust and carbon black are alike in that they both contain significant proportions of elemental carbon and trace amounts of polynuclear aromatic hydrocarbons (PNAs). Carbon fibers contain between 80 and 95% elemental carbon, while carbon black is essentially 88-99.5% elemental carbon. The small amounts of PNAs in each compound arise from the

pyrolysis of organic matter. PNAs are normally in concentrations of less than 0.1% in each (10,51).

The major effects of carbon black exposure are respiratory. Workers in carbon black manufacturing plants have experienced pneumoconiosis, pulmonary fibrosis, bronchitis, emphysema and tuberculosis. No reports of adverse health effects among carbon black user industries such as tire manufacturing and ink, plastic, and paint production, have been found (51).

Table 1

Organization	Standard	
	Total Dust (mg/m³)	Fibers (fibers/cc)
U.S. Coast Guard	10	-
U.S. Navy	3.5	3.0
ACGIH	10	-
OSHA	15	-
U.S. Air Force	10	-
Union Carbide	-	5

IV. METHODS

Sampling

The sampling strategy was focused on assessing worker total dust and carbon fiber exposure. Sampling was done at three potential exposure levels. The first exposure level, predicted to have the lowest concentrations, is the actual operation as it is now being performed. Under normal working conditions in the fiberglass shop, workers sanded composite hull components coated with a thin layer of primer. The second exposure level entails sanding composites only, again under normal working conditions in the fiberglass shop. This level represents a maximum exposure to carbon composite particulates under current working conditions. The third level is considered a worst case scenario. A sheet of carbon composite was sanded with a belt sander inside a 4 ft. high x 2 ft. wide x 5 ft. long plexiglass chamber. The chamber was equipped with a 5-inch axial flow fan, and was completely enclosed but for a 1 ft. x 2 ft. opening cut for handling the composite.

Procedures used were in accordance with methods outlined in the OSHA Industrial Hygiene Field Operations Manual (IHFOM) (52,53,54). For exposure levels 1 and 2, workers sampled wore MSA Model G personal sampling pumps with in-

line cassettes secured within two feet of the workers breathing zone. In chamber sampling, MSA Model G pumps pulled air through cassettes mounted on the walls of the chamber. All cassettes were within 3 feet of the sander.

Cassettes used in fiber sampling contained 0.8 micron pore size mixed cellulose ester filters. Filters with diameters of 25 mm and 37 mm were used and fiber sampling was done open-faced. Total dust samples were collected on a low-ash polyvinyl chloride filter that had been pre-weighed. Each pump was calibrated at 2.0 liters per minute using a bubble meter, and recalibrated after each sampling day. Consecutive samples were taken during the operation, and pump flowrates were checked periodically.

Several total dust samples were collected for the purpose of observing them with an optical microscope to determine the physical nature of the carbon composite debris. A particle size distribution, mean and median particle diameters, and the geometric standard deviation were developed for the composite particulates. Fibrous particles were examined to quantify a fiber:sphere particulate ratio and histograms of frequency versus fiber diameter and length.

Analytical Methods

Gravimetric total dust samples were weighed according to IHFOM guidelines (55). Fiber count analysis was done using the phase contrast optical microscopy technique, approved by

NIOSH for asbestos fiber counting. All fibers in one hundred grids are counted. A fiber is defined as a particle with a length-to-diameter ratio of 3:1, or greater (56).

The particle size analyses were done with an optical microscope at 500 x magnification. The cumulative distribution curve was generated from data obtained through stratified counting techniques. Projected diameters were used as equivalent diameters in sizing irregular particles. Fiber dimension measurements were derived by superimposing a porton graticule over a field of fibers. The graticule was calibrated with a stage micrometer (57).

V. RESULTS AND DATA ANALYSIS

Total Dust

Estimate of total dust exposure at the three exposure levels are shown in Table 2.

Table 2

Average Total Dust Concentrations

Exposure Level	Average Concentration (mg/m^3)	Range (mg/m^3)	Number of Samples
1-actual	1.89	1.15-2.81	8
2-composite only	17.8	5.7-31.63	4
3-chamber	47.2	31.9-96.62	7

Note: See Appendix 1 for individual sample data.

The average concentration for the actual operation (exposure level 1) is below both the Coast Guard standard $(10 \ mg/m^3)$ and the carbon black standard $(3.5 \ mg/m^3)$. The upper confidence 95% limit also indicates compliance with these standards (Appendix 3). Concentrations at exposure levels two and three are above both standards. Lower confidence limit calculations verify this (Appendix 3).

As the ranges indicate, the dust levels were highly variable at exposure levels two and three. A larger sample

size would reduce this variability. This is particularly evident in the "composite only" sanding exposure levels. A wide disparity exists in the results of the four samples taken, with two samples at the upper limit of the range and two at the lower limit.

The samples with the higher concentrations were taken in cassettes secured to the right side of the worker's collar. This irregularity is believed to be due to the swarf of the hand tool being directed toward the right shoulder of the tool operator.

The optical microscopy of particle size indicates that 97% of the particles sampled were in the respirable size range (0-10 microns). The distribution had a count mean diameter of 3.38 microns and a count median diameter of 2.55 microns. The geometric standard deviation was 2.04. Figure 6 is a cumulative frequency distribution curve of the sampled dust.

Carbon Fibers

Estimates of carbon fiber exposure at the three exposure levels are shown in Table 3.
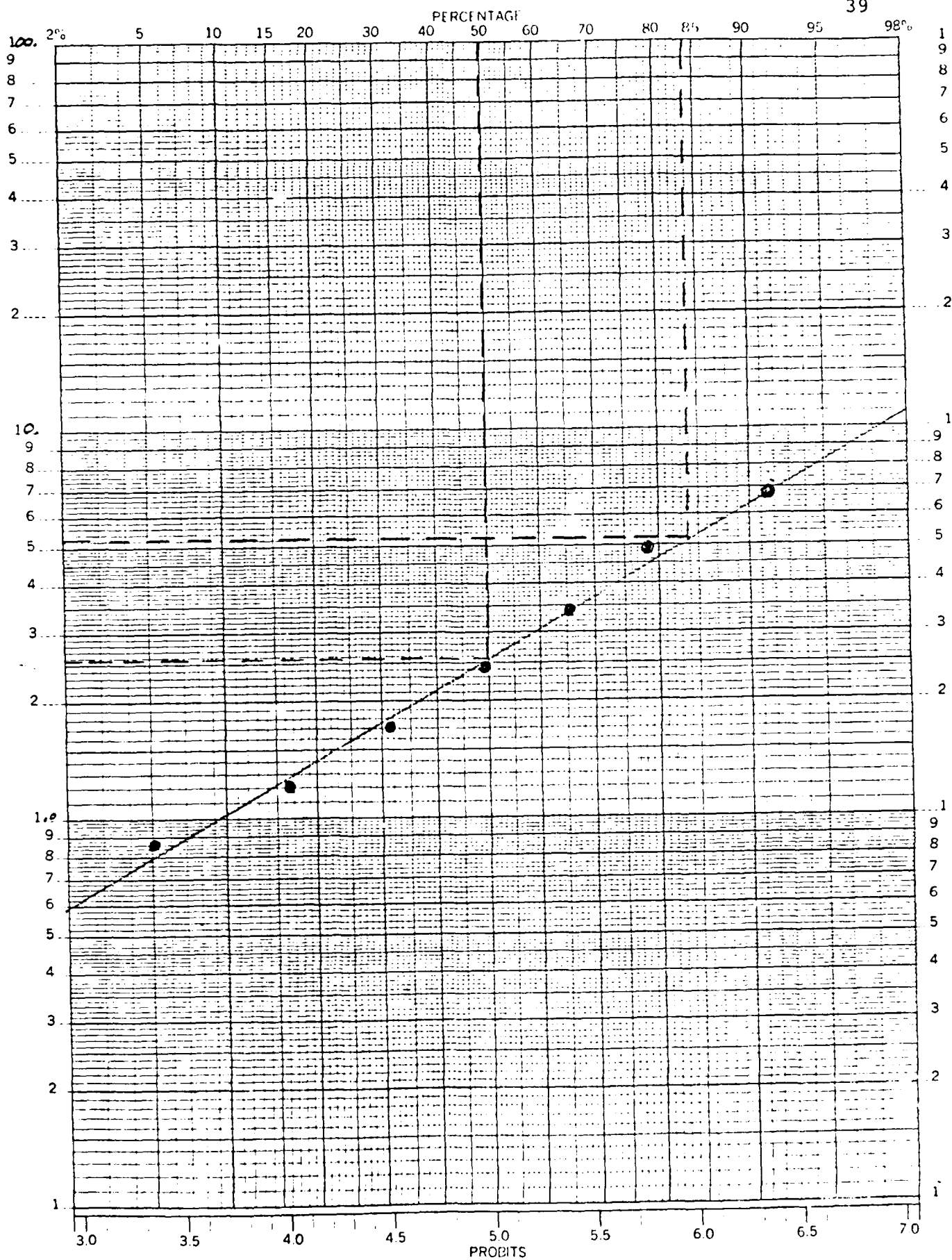
Figure 6. Cumulative frequency distribution.

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Table 3

Average Carbon Fiber Concentrations

Exposure Level	Average Concentration (fibers/cc)	Range (fibers/cc)	Number of Samples
1-actual	.055	0 - .07	2
2-composite only	.12	0 - .24	3
3-chamber	.24	0 - .5	5

Note: See Appendix 1 for individual sample data.

Average concentrations listed are not true averages.
When sample fiber counts are low, as is the case here, count
values are reported as being less than a given value, or a
range within a sample is given. The average concentrations
above were constructed using the range midpoints and the
upper limit of "less than" values.

The fiber concentrations at all exposure levels are very
low. When compared with the 3 fibers/cc fiberglass
standard, exposures during the actual operation were 55
times as low as the standard and the "worst case" chamber
concentrations were less than one-twelfth the standard.
Because of the imprecision of the sampling results, upper
confidence limits could not be calculated for carbon fiber
samples.

The optical microscopy analysis of fiber dimensions
confirms the results of Wagman et al. who reported that
machined carbon fibers had longitudinally cleaved. Analysis
shows that only 37% of the fibers observed had a diameter of

7 microns. The remaining 63% of the fibers had diameters of less than 7 microns, indicating that 7 micron fibers had been cleaved. Forty-nine per cent of the fibers observed had diameters less than 3.5 microns. The count mean fiber diameter is 3.76 microns. Fiber diameters are graphically represented in Figure 7.

Fiber lengths ranged from 2.5-55 microns with a count mean length of 14.95 microns. The majority of the fibers were at or near a 3:1 length-to-diameter ratio. No fiber had an aspect ratio greater than 8:1. Figure 8 is a histogram depicting frequency of fiber lengths.

Fiber:Sphere Ratio

By count, spheres outnumbered fibers by approximately 27:1. Of the 114.4 particles per field observed in stratified counting, 110.25 were spheres and 4.15 were fibers.
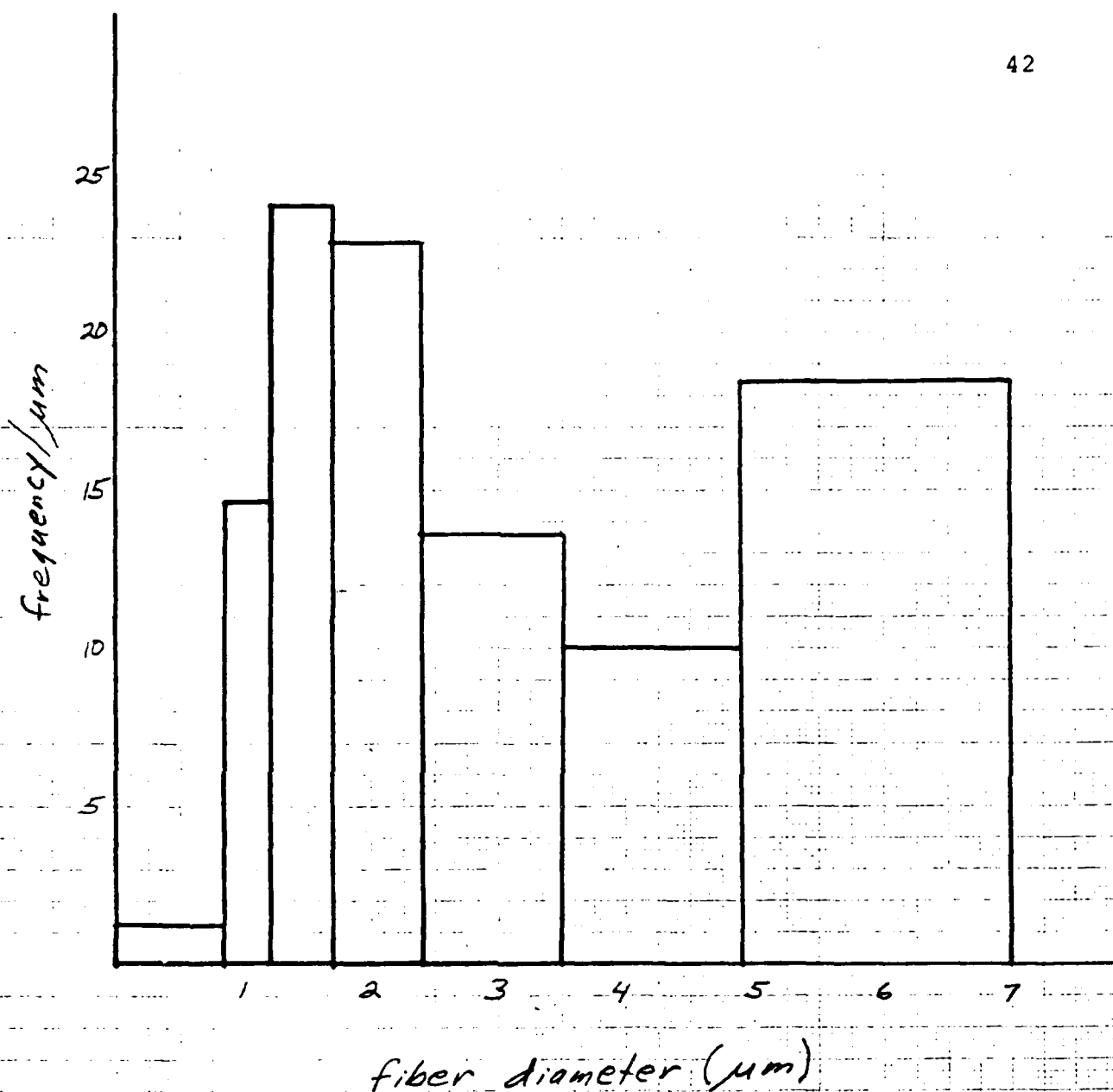
frequency of fiber diameters after sanding

figure 7

note: See Appendix 2 for grouped data
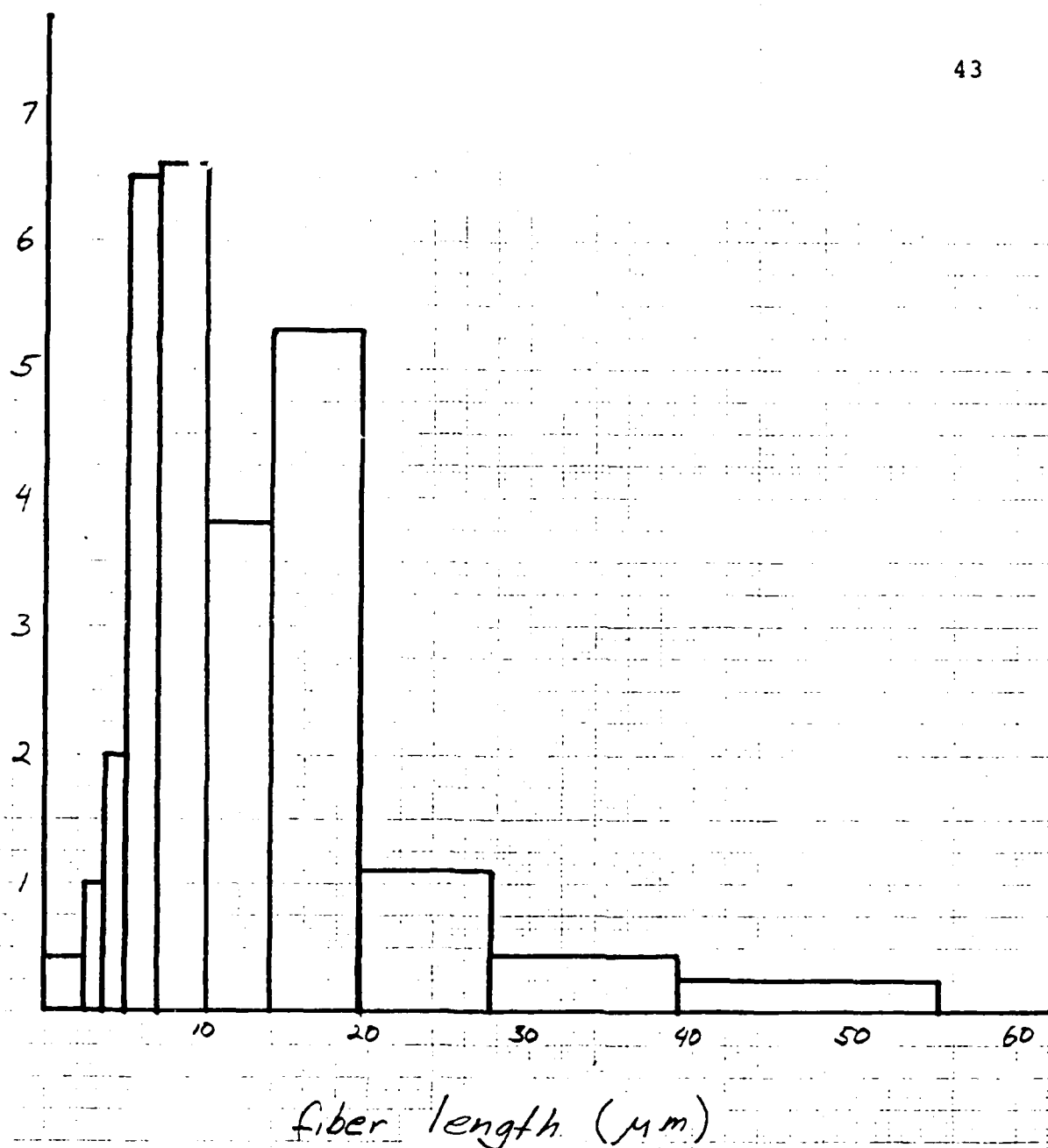
fiber length (μm)

frequency of fiber lengths after sanding

figure 8

note: see Appendix 2 for grouped data

VI. CONCLUSIONS

From analysis of the data, it can be concluded that
total dust and fiber concentrations being generated during
carbon composite sanding operations at the U.S. Coast Guard
Aircraft Repair and Supply Center do not exceed current
Coast Guard standards. However, it may also be concluded
that present standards may not adequately safeguard exposed
workers for the following reasons:

1. Results of this report indicate that carbon fibers
    cleave longitudinally, thereby generating fibers of
    a more respirable size.

2. Potentially carcinogenic compounds, polynuclear
    aromatics, are present in the fibers and dust.

3. Because the development and use of carbon fibers is
    still relatively new, no chronic human data exists.

Sampling results indicate that personnel total dust
exposure during actual (exposure level 1) sanding operations
are below the TLV. Average composite-only sanding (exposure
level 2) dust levels, however, were significantly above the
TLV. It is recommended that further air sampling be done
should the nature of composite machining change so that

greater concentrations of composite debris are being generated.

In light of the lack of substantiating evidence for carbon fiber or carbon composite dust standards, good industrial hygiene work practices dictate that exposure levels be kept to a minimum.

VII. RECOMMENDATIONS

Work Area

It is recommended that no machining of carbon composite materials be done in an open hangar area. There are several reasons for this caution. General exhaust ventilation is the only form of ventilation in the hangars. Dilution ventilation is considered inadequate for removal of particulates from workplace air, and the large dimensions of the hangar make it less efficient (59). Secondly, quite a few employees, upwards of 50 in number, either work in or pass through the hangar in the course of the workday and are thereby exposed to composite dust and fibers. While this dose may be low, these employees are generally unprotected.

The fiberglass shop, where most composite work is currently being done, is better than the open hangar, but potential hazards remain. Fewer employees are being contaminated in the fiberglass shop. During each occasion when sampling was done, two workers other than those sanding carbon composites were present. One worker was sanding and grinding fiberglass and the other was painting. Neither worker wore adequate skin or eye safeguards. The painter wore no respiratory protection.

The ventilation in the fiberglass shop is inadequate. The system consists of two painting booths and a small volume of make-up air. The filters in the paint booths have been removed because they were quickly saturated by the large dust concentration being generated. Only the metal grid frames remained in the booths. Composite machining operations have been shut down in the past by supervisors because of a lingering dust cloud. A test of the ventilation system was performed by lighting a 30-second smoke candle in the vicinity where the machining operation is performed. The smoke cloud lingered without movement until a door was opened. Upon opening the door the smoke cloud rushed towards the paint booth, clearly indicating a shortage of make-up air.

Ideally, composite machining operations should be done in a shop dedicated exclusively to this operation. The composite shop should be composed of two rooms, a "clean" room and a "dirty" room. The clean room is where lay-up work involving the use of solvents is to be done. Suitable ventilation for the removal of solvents should be utilized. The dirty room is where the machining of composites will take place. Ventilation of the dirty room will be discussed later. Personnel in the composite shop should also have access to lockers and showers to ensure that workers and their clothing are not contaminated when they leave the work area (49).

Controls

It is recommended that several forms of control intended to reduce workplace exposure to carbon composite materials be implemented. These include personal protective equipment, ventilation, improved housekeeping, sanitation, five hazard minimization, and administrative controls.

Since large amounts of dust are being generated, and significant skin exposure is anticipated, personnel engaged in machining operations should wear clothing that precludes skin contamination. Disposable long-sleeved coveralls are best. Coveralls offer nearly full-body protection, and the disposable variety eliminates the possibility of exposures during laundering operations (58). A hood which covers the head, excluding the face, should be worn. Coveralls which have incorporated hoods are the optimum. Again, the disposable type are preferable. For eye protection, safety glasses with side shields should be required for all composite machining operations. The safety glasses may be supplemented with a full length face shield when warranted by the specific operation. Gloves should be worn to act as a fiber and dust barrier (58). A glove should be selected that prevents the penetration of composite splinters while not severely limiting the manual dexterity of the machine operator. It may also be necessary to require the use of disposable shoe coverings. Should workers need to enter other work areas, the coverings should be removed to prevent the tracking of dust and fibers.

The "dirty" room will utilize local exhaust ventilation to remove composite particulates thereby reducing personnel exposure. Since the removal of particulates by local exhaust ventilation systems is relatively inefficient, exhaust hood designs where air flow is drawn from under a sanding operation is preferable. The portable hand grinding booth and the portable chipping and grinding table shown in Appendix 5 are examples. If possible, the use of a high velocity, low-volume exhaust system which would attach directly to the tool would also be effective. This type of ventilation controls the dust from portable hand tools by exhausting air directly at the point of dust generation using close-fitting, custom-made hoods. A low volume-high velocity exhaust system for a disc sander is also pictured in Appendix 5 (59).

An effective means of dust control other than ventilation is through the use of plastic bags. Plastic fiber (polyester, nylon) bags can be designed to fit around or near the tool while in use to collect particles as they are being generated (36).

For the levels of exposure of the magnitude measured in this report, dust masks are adequate respiratory protection. Should airborne concentrations of fibers increase however, the NIOSH respirator selection guide for fibrous glass (Appendix 4) should be consulted. Recommended respirator types range from a dust and mist respirator for the lowest concentration (<15 fibers/cc) to a positive pressure self

contained breathing apparatus for extremely high exposures
(>3000 fibers/cc). When very small composite particulates
in the 0.5 to 1.0 micron range are generated, the use of
High Efficiency Particulate Air (HEPA) filters should be
considered (58).

A form of control that can eliminate significant
proportions of dust and fibers, and should not be ignored,
in general housekeeping. The simplest and most effective
way to keep the work area clean and free of dust is with a
high efficiency vacuum system, capable of extracting
particles in the 0.5-1.0 micron size range (49). In
addition to the work area, the worker's clothing and the
worker himself should also be vacuumed after each exposure
(49). The use of compressed air to blow dust off workers is
prohibited as the resuspension of dusts from the blast of
air would contribute to the exposure of other personnel
(58).

Good personal hygiene of workers involved with carbon
composite machining should be encouraged and facilitated by
management. Handwashing stations suitable for removing
carbon composite debris from the skin should be provided.
Hands, arms, and face should be thoroughly washed prior to
eating and at the end of each shift. Food should not be
stored, prepared, dispensed, or eaten in composite work
areas. Again, showers and a locker area are highly
recommended (49).

To minimize the danger of fire, solvents should be used only in the clean room and stored in approved containers. Quantities of solvents on hand should only satisfy immediate needs. All sources of flames, smoking, and other sources of ignition should be eliminated from the work area. Only spark-proof tools should be used. Static electricity can be minimized by grounding all electrical machinery (36).

Possibly the most effective controls that can be implemented are administrative. Administrative controls included training, modification of work practices, posted warnings, and enforcement.

Upon assignment to jobs involving the machining of carbon composite materials, workers should be informed of the hazards, symptoms of overexposure, procedures to follow in the event of an emergency, and precautions to be taken to ensure safe use of the composite material and to minimize exposure. Information pertaining to the toxicity of the material should be acquired and made available to those personnel who are potentially occupationally exposed. Manufacturers' material safety data sheets should be provided to personnel as part of an education program. An ongoing training program should be conducted by instructors qualified in specific areas. The purpose of the training is to ensure that personnel have current knowledge of job hazards and proper maintenance and cleanup methods, and that personal protective equipment and respirators are being used effectively. Exposed workers should also be told about the

intent and reasons for a medical monitoring program (to be discussed later) and its advantages (49). The modification of work practices could be accomplished through training. An important example would be the redirection of the hand tool swarf during sanding operations. Caution signs should be posted at all entrances to the carbon composite work area to eliminate the possibility of unnecessary exposure of workers from other shops. The sign should warn personnel of the potential hazard inside (50). The enforcement of safety rules is largely a matter of education. Workers must understand safety requirements and the reasons for following them.

A spirit of cooperation and mutual understanding between worker and management often makes enforcement unnecessary. When a worker continually performs unsafe acts which endanger the health and safety of himself and others, however, appropriate action must be taken or the rules will be interpreted as being meaningless.

Medical Monitoring

Personnel exposed to carbon composite particulates should be enrolled in the Coast Guard Occupational Medical Monitoring Program (45). In addition to program requirements, the following medical surveillance measures should be implemented:

1. Preplacement

   a. Medical history, including acute and chronic skin and respiratory conditions, and allergies.

   b. Previous occupational exposure to dusts such as coal, silica and asbestos.

   c. Physical examination with emphasis on skin and respiratory system.

   d. Specific testing

      1) pulmonary function (forced vital capacity and one-second forced vital capacity)

      2) chest x-ray

2. Periodic testing (annual with exception of chest x-ray)

   a. interim medical history

   b. interim occupational history

   c. physical examination with emphasis on skin and respiratory system and allergies.

   d. specific testing

      1) pulmonary function (FVC and FEV_1)

      2) chest x-ray (every three years)

(49)

Waste Disposal

Carbon composite waste should not be disposed of by conventional means. After composite debris has been collected, the waste fibers and dust should be packaged and disposed of in landfills authorized to accept wastes of this nature. Little is known about the fate of carbon composite scrap and debris when it is buried. Carbon fibers should never be incinerated. Documented reports have shown that

incineration decreases particle diameter, thereby increasing the public health risk (58).

Standards

In light of toxicological and chemical evidence gleaned from the literature and the results of this report, I recommend that the Coast Guard adopt a carbon fiber standard of 3 fibers/cc and a total composite dust standard of 3.5 mg/m^3.

The present standard of 10 mg/m^3 for carbon composite debris assumes that it is merely a nuisance dust. Nuisance dusts are described as "biologically inert" dusts that have a long history of little adverse health effect on lungs and do not produce significant organic disease or toxic effect (46). For some time, carbon fibers have been considered merely a nuisance particulate based on the assumptions that (1) carbon composite is composed of elemental carbon and elemental carbon is inert, and that (2) carbon fibers exist only with diameters greater than 3.5 microns, out of the respirable range.

While it is true that carbon composite materials are composed mainly of elemental carbon, other compounds, some potentially harmful, are included. Clearly, a substance with constituents such as polynuclear aromatic hydrocarbons, even in minor proportions, cannot be dismissed as merely a nuisance.

The popular theory is that the thinner a fiber is, the greater potential for carcinogenicity is has, at least in regard to mesotheliomal tumors (61). Since this paper confirms the report of Wagman et al. that fibers in the respirable range are being generated, embracing the possibility that carbon fibers may be toxic and could produce significant organic disease would be the prudent basis for action.

Further Work

Much work remains to be done in the area of carbon composite materials. Generally, competent evidence is needed to substantiate a lower carbon composite debris standard. Detailed analyses of various carbon composites need to be done to more precisely quantify the chemical make-up of composites and the variation in chemistry that exists between products. Carbon fiber and composite production processes should be analyzed to assess the source of chemical variation with the intent of eliminating hazardous constituents. Animal studies of the inhalation of sized respirable carbon fibers need to be initiated to gain a greater understanding of the toxicology of carbon fibers.

On a a local scale, the proposed clean room at the Aircraft Repair and Supply Center should be sampled for solvent vapors during lay-up operations. Further investigations into paint primer particles is also warranted.

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APPENDIX 1

TOTAL DUST AND FIBER CONCENTRATIONS FOR EACH FILTER

Total Dust

		Exposure Level 1 - Actual		
Filter #	Conc. (mg/m^3)	Sample Time (mins)	Total wt. (mg)	Comments
M022587C	1.25	960	1.2	full period single
M022587D	1.77	"	1.7	"
J022587A	1.56	"	1.5	"
J022587B	1.15	"	1.1	"
J022687A	1.77	"	1.7	"
J022687B	2.08	"	2.0	"
M022687C	2.71	"	2.6	"
M022687D	2.81	"	2.7	"
04200	<2.5	20	<0.1	1/2 exposure

		Exposure Level 2 Composite Only		
Filter #	Conc. (mg/m^3)	Sample Time (mins)	Total wt. (mg)	Comments
0420D	.35	96	.067	1/2 exposure
0420I	31.63	43	2.72	right shoulder
0420J	7.8	43	0.67	left shoulder
0420K	23.3	35	2.2	right shoulder
0420L	5.7	35	0.4	left shoulder

Exposure Level 3 – Chamber

Filter #	Conc. (mg/m^3)	Sample Time (mins)	Total wt. (mg)	Comments
0417E	41.21	19	1.57	
0417F	34.61	19	1.32	
0417G	31.9	36	2.3	
0417H	34.7	36	2.5	
0417I	47.2	36	3.4	
0417L	96.29	7	1.82	in swarf
0417M	96.62	7	1.69	in swarf

Carbon Fibers

Exposure Level 1 – Actual

Filter #	Conc. (fibers/cc)	Sample Time (mins)	Comments
0420M	<.04	41	
0420N	<.07	41	

Exposure Level 1 – Actual

Filter #	Conc. (fibers/cc)	Sample Time (mins)	Comments
0420A	–	–	overloaded
0420B	–	–	overloaded
0420C	.02+.02	9	1/2 exposure
0420E	<.09	33	
0420E	<.2417	28	
0420G	–	–	overloaded
0420H	–	–	overloaded

Exposure Level 3 – Chamber

Filter #	Conc. (fibers/cc)	Sample Time (mins)	Comments
0417A	<.07	19	
0417B	.07±.07	"	
0417C	.07±.07	"	
0417Y	<0.5	7	
0417Z	<0.5	"	

APPENDIX 2

GROUPED DATA FOR SIZE DISTRIBUTIONS

Size Range (um)	Count (n) (particles/ field)	Midpoint Diameter	Cum #	Cum %	Mdpt. x (n)
0-.61	0	.305	0	0	0
.61-.86	6	.74	6	5.2	4.44
.86-1.2	13	1.03	19	16.6	13.39
1.2-1.7	17	1.45	36	31.5	24.65
1.7-2.4	21	2.05	57	49.8	43.05
2.4-3.5	18	2.95	75	65.6	53.10
3.5-4.9	15	4.2	90	78.7	63.0
4.9-6.9	15	5.9	105	91.8	88.50
6.9-9.8	5.6	8.35	110.6	96.7	46.76
9.8-13.8	2.8	11.8	113.4	99.1	33.04
13.8-19.6	1	16.7	114.4	100	16.7
>19.6	0		114.4		

114.4

- Count mean diameter = $\dfrac{\Sigma \, n_i d_i}{N}$ = 3.38 um

- Count mean diameter (from Figure 6) = 2.55 um

- Geometric standard deviation = $\sigma_g = \dfrac{84\%}{50\%}$ = 2.04
  (from Figure 6)

Fiber Diameter Distribution

Size Range (um)	(n) Count	Frequency/um	%	Cum %	Mid-Point	Mdpt. x n
0-.86	1	1.16	1	1	.43	.43
.86-1.2	5	14.7	5	6	1.03	5.15
1.2-1.7	12	24.0	12	18	1.45	17.4
1.7-2.4	16	22.9	16	34	2.05	32.8
2.4-3.4	15	13.6	15	49	2.9	43.5
3.4-4.9	14	10.0	14	63	4.15	58.1
4.9-6.9	37	18.5	37	100	5.9	218.3
	100					

$$- \text{Count mean diameter} = \frac{\Sigma\, n_i d_i}{N} = 3.76 \text{ um}$$

Fiber Length Distribution

Size Range (um)	(n) Count	Frequency/um	Cum %	Mid-Point	Mdpt. x n
0-2.4	1	.42	1	1.2	1.2
2.4-3.4	1	1.0	2	2.9	2.9
3.4-4.9	3	2.0	5	4.15	12.45
4.9-6.9	13	6.5	18	5.9	76.7
6.9-9.8	19	6.6	37	8.4	159.6
9.8-13.8	15	3.8	52	11.8	177.0
13.8-19.5	30	5.3	82	16.65	499.5
19.5-27.5	9	1.1	91	23.5	211.5
27.5-39.0	5	.43	96	33.25	166.25
39.0-55.0	4	.25	100	47	188.0
>55.0	0	0			

$$- \text{Count mean length} = \frac{\Sigma\, n_i d_i}{N} = 14.95 \text{ um}$$

APPENDIX 3

UPPER/LOWER CONFIDENCE LIMITS

Method of Calculation

- For full period single sample measurements
  (Exposure Level 1)

  $\bar{X}$ = Average Concentration

  STD = Standard

  CV_T = .05 (for total dust sampling/analytical)

  $$x = \frac{\bar{X}}{STD}$$

Upper Confidence Limit (95%) = $x + (1.645)(CV_T)$

If UCL ≤ 1, classify as compliance exposure

  UCL > 1, classify as possible over-exposure

- For partial period consecutive samples measurements
  (Exposure Levels 2 and 3)

  x = sample concentration

  t = sample time

  STD = standard

  CV_T = .05 (for total dust sampling/analysis)

  $$TWA = \frac{(Xt)}{t}$$

Lower Confidence Limit (95%)

$$= \frac{TWA}{STD} - \frac{1.645(CV_T) \quad t^2}{t}$$

If LCL >1, classify as non-compliance exposure

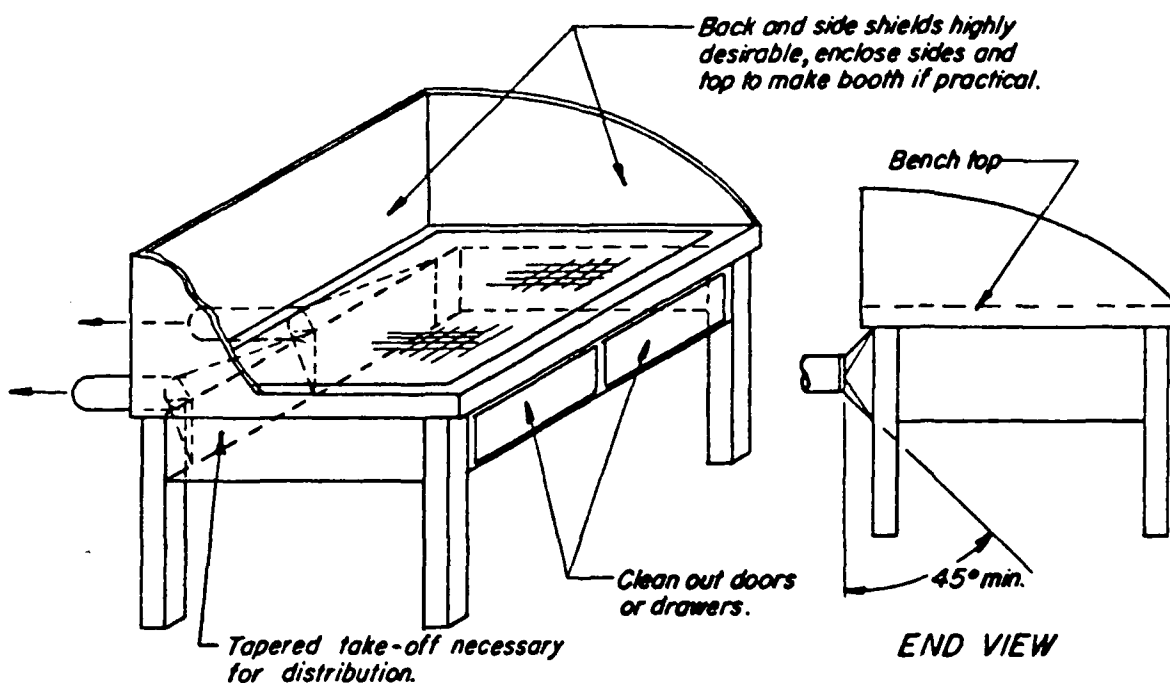LCL $\leq$ 1, classify as possible over-exposure

APPENDIX 4

RESPIRATOR SELECTION GUIDE FOR CARBON FIBERS

Carbon Fiber Concentration	Respirator Type
Less than or equal to 15 fibers/cubic centimeter	(1) A dust and mist respirator (change filter frequently)
Less than or equal to 30 fibers/cc	(1) A dust and mist respirator single-use or quarter-mask respirator; or (2) A high efficiency particulate filter respirator; or (3) A supplied-air respirator; or (4) A self-contained breathing apparatus.
Less than or equal to 150 fibers/cc	(1) A high-efficiency particulate filter respirator with full facepiece; or (2) A supplied-air respirator with a full facepiece, helmet, or hood; or (3) A self-contained breathing apparatus with a full facepiece.
Less than or equal to 300 fibers/cc	(1) A powered air-purifying respiratory with a high efficiency particulate filter and full facepiece; or (2) A type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous flow mode.

Greater than 300 fibers/cc

(1) A combination respirator which includes a type C supplied-air respirator operated in pressure-demand or continuous flow mode; or

(2) Self-contained breathing apparatus with full facepiece, pressure-demand or other positive pressure mode.

APPENDIX 5

VENTILATION SYSTEMS

Back and side shields highly
desirable, enclose sides and
top to make booth if practical.

Bench top

Clean out doors
or drawers.

Tapered take-off necessary
for distribution.

45° min.

END VIEW

Q = 150 - 250 cfm/sq ft of bench area.
Minimum duct velocity = 3500 fpm
Entry loss = 0.25 VP for tapered take-off.

Grinding in booth, 100 fpm face velocity also suitable.

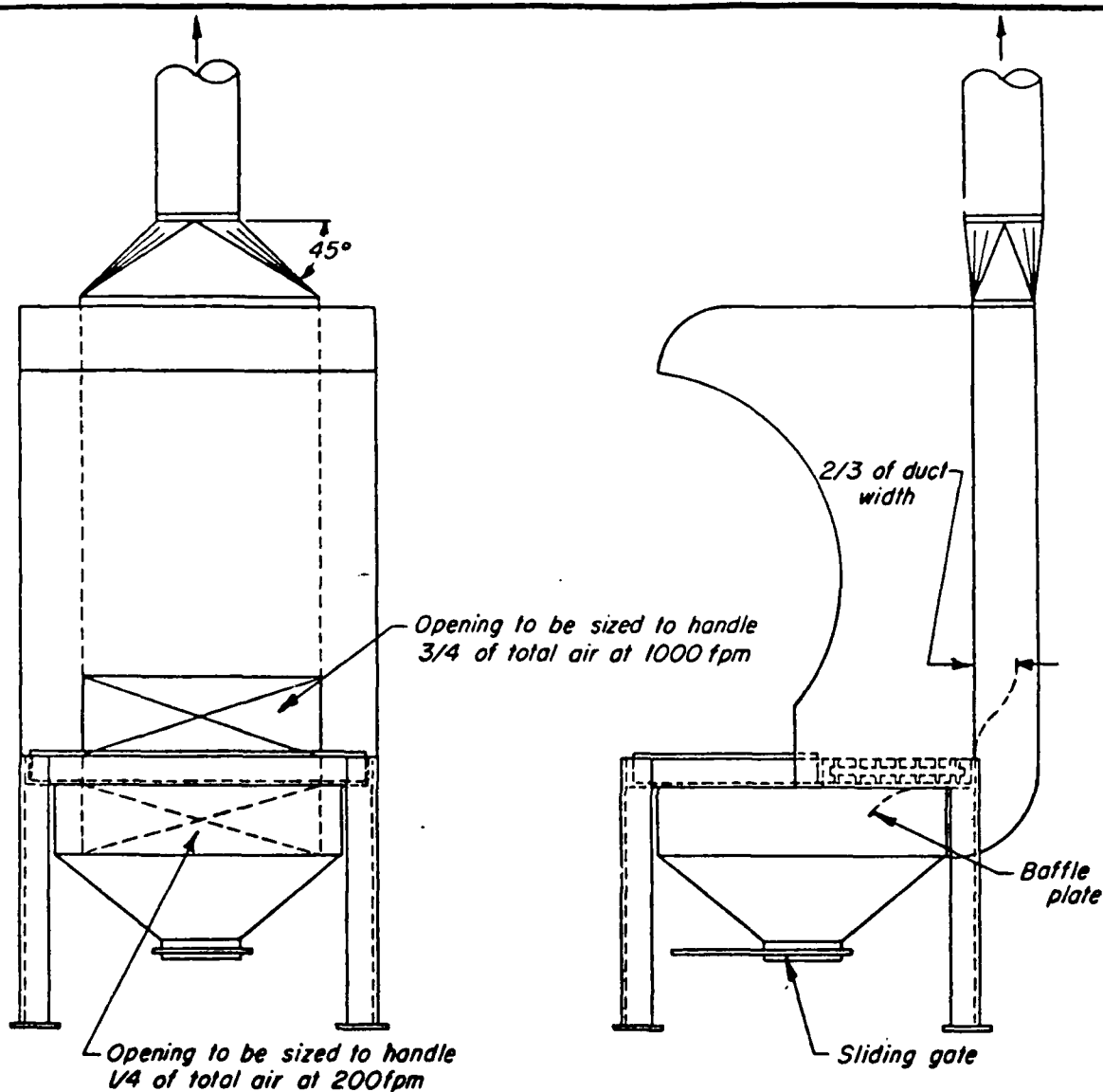For downdraft grilles in floor: Q = 100 cfm/sq ft of working area.

Provide equal distribution. Provide for cleanout.

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PORTABLE HAND GRINDING	
DATE 1-64	VS-412

45°

Opening to be sized to handle
3/4 of total air at 1000 fpm

2/3 of duct width

Baffle plate

Opening to be sized to handle
1/4 of total air at 200 fpm

Sliding gate

Q = 150 cfm/sq ft of hood face
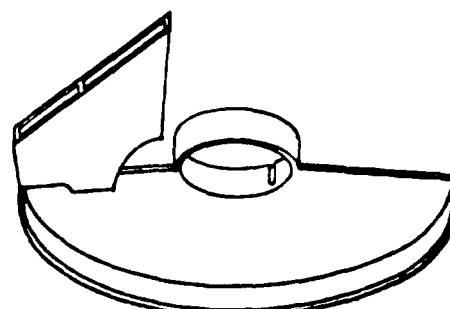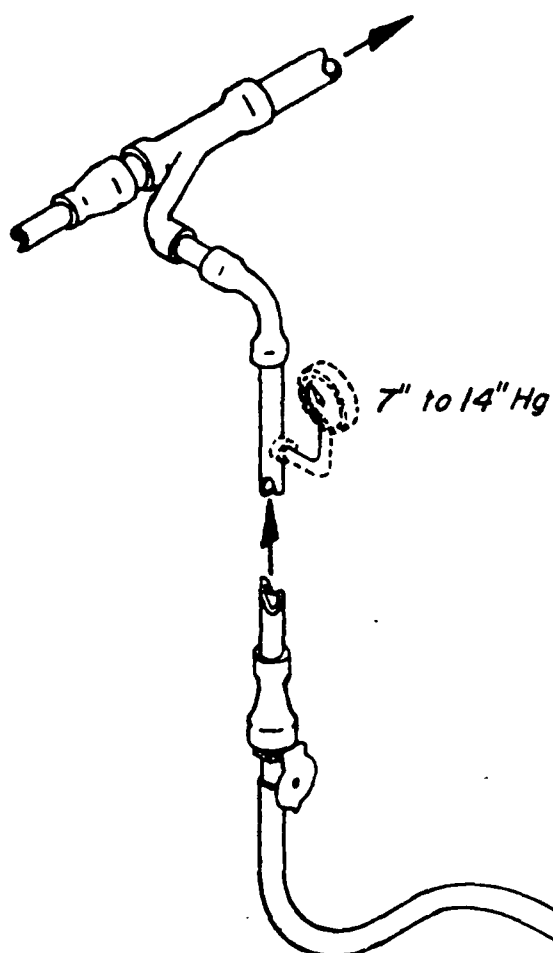Duct velocity = 3500 fpm
Entry loss = 0.25 VP

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PORTABLE CHIPPING AND GRINDING
TABLE

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Bottom view of
extractor hood

7" to 14" Hg

Q = 10-30 cfm/inch dia
Branch static pressure = 7"to 14"Hg
Slot velocity = 24,000 to 39,000 fpm
Flexible hose = 1" to 2" ID
Extension hose = Up to 8 ft long*

Sanding disc size = 2" to 9" dia

Peripheral speed = 4,500 -14,000 linear fpm

*Hose lengths may be extended up to a
maximum of 50' by using
larger sizes between the tool
hose and the tubing system.
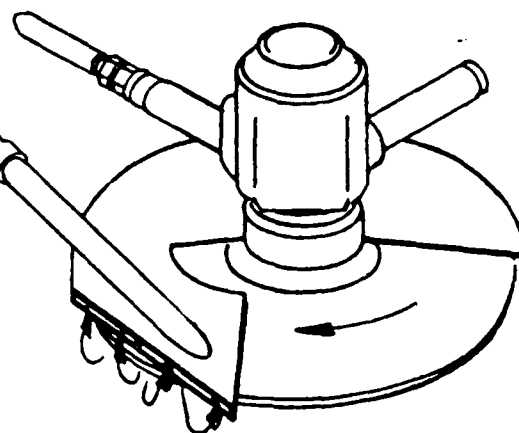
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EXTRACTOR HOOD FOR DISC SANDER

Reference 74

| DATE | 1-78 | VS-805 |

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